

# Volatile Organic Compounds Analysis in Drinking Water with Headspace GC/MSD Using Hydrogen Carrier Gas and HydroInert Source



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## Abstract

An Agilent 8890/5977C GC/MSD system coupled with an Agilent 8697 headspace sampler was successfully used with hydrogen carrier gas for the analysis of volatile organic compounds (VOCs) in drinking water. Recent concerns with the price and availability of helium have led laboratories to look for alternative carrier gases for their GC/MS methods. For GC/MS, hydrogen is the best alternative to helium, and offers potential advantages in terms of chromatographic speed and resolution. However, hydrogen is not an inert gas, and may cause chemical reactions in the mass spectrometer electron ionization (EI) source. This can lead to disturbed ion ratios in the mass spectrum, spectral infidelity, peak tailing, and nonlinear calibration for some analytes. Therefore, a new EI source for GC/MS and GC/MS/MS was developed, and optimized for use with hydrogen carrier gas. The new source, named HydroInert, was used in the system evaluated here. In addition to the new source, the chromatographic conditions were optimized to provide separation of 80 volatile compounds in 7 minutes. Standards and samples were analyzed in both scan and SIM data acquisition modes. For the scan data, spectra were deconvoluted with MassHunter Unknowns Analysis software and searched against NIST 20 to assess the spectral fidelity. In both modes, quantitative calibration was performed for the 80 compounds over the range of 0.05 to 25  $\mu\text{g/L}$ . As demonstrated in this note, the system gives excellent results for the analysis of VOCs in drinking water.

## Introduction

One of the analyses commonly used to ensure that the quality of drinking water is the measurement of volatile organic compounds (VOCs). These compounds can appear in drinking water by contamination from numerous sources, including industrial and commercial operations. Another common source is when VOCs are formed by the addition of chlorine (used to disinfect the water), and react with natural organic matter in the source water. Regulations governing the allowable concentration of VOCs in drinking water vary by country and region, but are typically in the low  $\mu\text{g/L}$  (ppb) range. Due to the large number of potential contaminants, and the need to measure them at such low levels, GC/MS systems are commonly used. GC/MS offers both the sensitivity and selectivity required to identify and quantify VOCs. Purge and trap<sup>1</sup> and static headspace<sup>2,3</sup> are two commonly used automated sampling techniques that extract the VOC analytes from water samples and inject them into the GC/MS. This application note describes a system configured to perform static headspace/GC/MS analysis of VOCs in drinking water, optimized for using hydrogen as the carrier gas.

The system configured here was optimized for hydrogen carrier use, employing the following key components and techniques:

- Agilent J&W DB-624 Ultra Inert column: The DB-624 UI column, 20 m  $\times$  0.18 mm, 1  $\mu\text{m}$  (part number 121-1324UI) is designed to provide high chromatographic resolution of VOCs when using hydrogen carrier gas. This allowed the separation of 80 VOCs in under 7 minutes.
- The Agilent Inlet Liner, Ultra Inert, splitless, straight 1 mm id (part number 5190-4047) is necessary to connect the transfer line from the headspace unit to the GC column in the inlet. Use of wider inner diameter liners can cause broadening of analyte peaks with low split ratios like that used here.
- Pulsed split injection: Pulsed split injection is helpful in getting the injection bandwidth narrow enough to be compatible with the small diameter column used here. The technique allows a low split ratio, such as 21:1 used in this study, to maintain sensitivity while providing a high split flow during the injection, to rapidly sweep the headspace sample loop. Rapid sweeping of the loop is key to reducing peak broadening, especially for the earliest-eluting compounds.
- Agilent HydroInert source with 9 mm extractor lens: Because hydrogen is used as the carrier gas, the HydroInert source<sup>4</sup> is used. This new EI extractor source was developed and optimized for use with hydrogen carrier gas, and greatly reduces in-source reactions that can cause problems with spectral infidelity, peak tailing, and nonlinear calibration for some analytes like nitrobenzene.
- Spectral deconvolution with Agilent MassHunter Unknowns Analysis software: The Agilent Unknowns Analysis software uses spectral deconvolution to extract clean analyte spectra from those of overlapping peaks. This results in higher library match scores, and greater confidence in peak identifications. NIST20 was used as the reference library.
- Addition of salt: The addition of salts like sodium chloride or sodium sulfate to aqueous headspace samples is commonly used to increase sensitivity of the analysis. The presence of the salt increases the amount of a compound that partitions into the gas phase. Sodium sulfate was chosen for this work.

Both scan and SIM modes of data acquisition were evaluated. Scan is useful for confirming the identity of found targets, and for identifying nontarget compounds. It can also be used retrospectively to search for compounds that may become of interest in the future. SIM has a substantial advantage in the signal-to-noise ratio, and is preferred where quantitation to low levels is required.

## Experimental

The Agilent 5977C Inert Plus MSD was coupled to the Agilent 8890 GC equipped with a multimode inlet (MMI) and an Agilent 8697 headspace sampler. A HydroInert source (G7078-60930 for the fully assembled source with 9 mm lens) was used in the MSD, and autotuned using the etune tuning algorithm. The analytical method used an Agilent Ultra Inert straight-through 1.0 mm GC inlet liner (part number 5190-4047) and a DB-624 UI column, 20 m  $\times$  0.18 mm, 1  $\mu\text{m}$  (part number 121-1324UI). The 8697 Headspace Sampler was connected to the GC carrier gas inlet line between the GC control pneumatics and the GC injection port. A pulsed split injection was used with the split ratio set to 21:1.

Eight calibration levels ranging from 0.05 to 25  $\mu\text{g/L}$  were prepared in water by spiking 5  $\mu\text{L}$  of a corresponding stock solution (which also included the ISTD) into 10.0 mL of water in a 20 mL headspace vial. Five grams of anhydrous sodium sulfate were weighed into each vial before the addition of water

and spiking solution. After capping, each vial was vortexed vigorously for 20 seconds, before placement in the headspace sampler. The spiking stock solutions were prepared in methanol using an Agilent 73-compound standard (DWM-525-1), an Agilent six-compound gas standard (DWM-544-1), and an Agilent three-compound ISTD mix (STM-320N-1), containing fluorobenzene (internal standard), 1,2-dichlorobenzene-d4 (surrogate), and BFB (surrogate). The ISTD/surrogate mix was added to each calibration stock solution at a level to give 5 µg/mL of each compound in the water. Agilent MassHunter Workstation software was used for data acquisition and processing. Figure 1 shows the system configuration used here. The operating parameters are listed in Table 1.

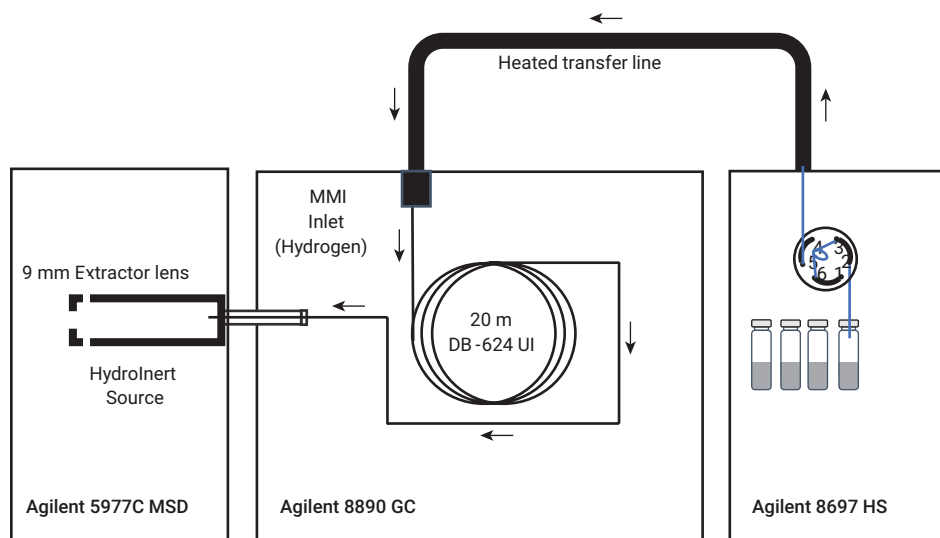


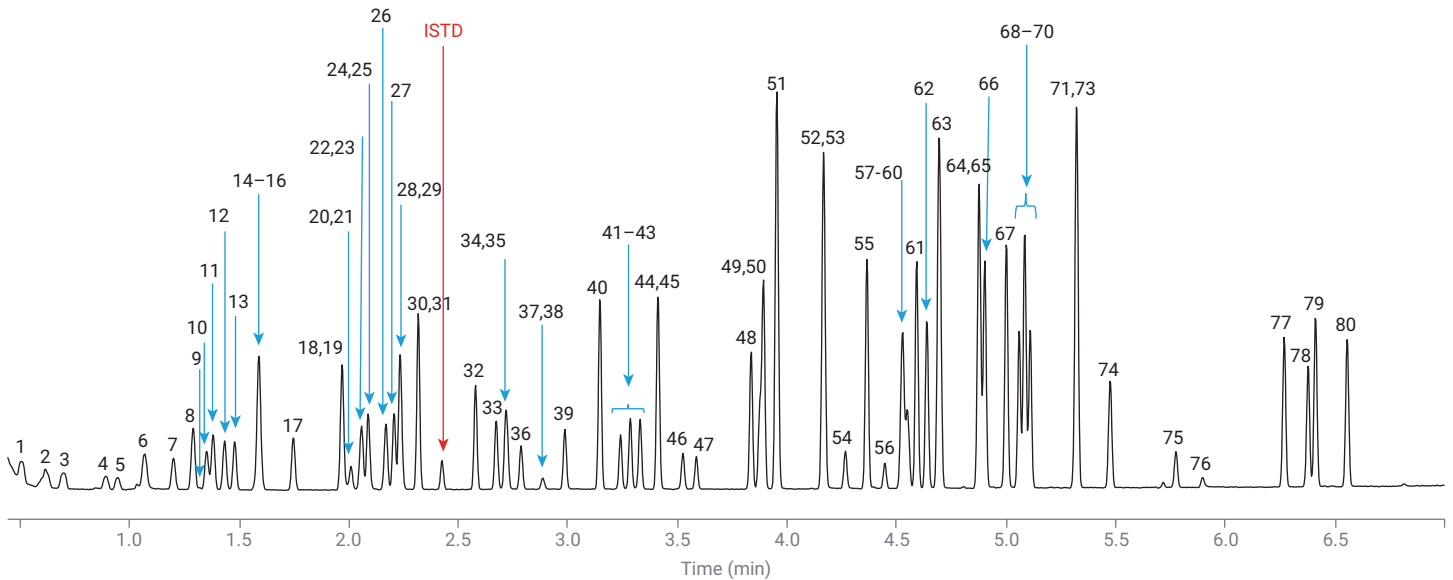
Figure 1. Instrument configuration.

Table 1. Gas chromatograph, mass spectrometer, and headspace sampler parameters for VOCs analysis.

Agilent 8890 GC Parameters		Agilent 8697 Headspace Sampler	
Parameters	Setpoints	8697 Loop Size	1 mL
Inlet Temperature	200 °C	Vial Pressurization Gas	Nitrogen
Liner	Agilent Ultra Inert inlet liner, splitless, straight, 1 mm id (p/n 5190-4047)	HS Loop Temperature	75 °C
Carrier Gas	Hydrogen	HS Oven Temperature	75 °C
Column Flow	0.95 mL/min constant flow	HS Transfer Line Temperature	115 °C
Injection Mode	Pulsed split	Vial Equilibration	12.00 min
Split Ratio	21:1	Injection Duration	0.30 min
Pulse Pressure	26 psig until 0.3 min	GC Cycle Time	15.00 min
Septum Purge Flow	3 mL/min	Vial Size	20 mL
Column	Agilent DB-624 Ultra Inert, 20 m × 0.18 mm, 1 µm (p/n 121-1324-UI)	Vial Shaking	Level 9, 250 shakes/min with acceleration of 980 cm/s <sup>2</sup>
Oven Program	35 °C (0.25 min), ramp 25 °C/min to 240 °C (0.2 min) Run time 8.65 min	Fill Mode	Default
Agilent 5977C MSD		Fill Flow	50
MS Source	HydroInert Extractor with 9 mm Extractor Lens	Fill Pressure	10 psi
MS Tune	Etune	Pressure Equilibration Time	0.1 min
MSD Transfer Line Temperature	250 °C	Postinjection Purge	100 mL/min for 2 min
MS Source Temperature	250 °C		
MS Quad Temperature	200 °C		
Scan Range	35 to 260 Da		
Scan Speed	A/D samples 4, TID on		
EM Gain Factor (Scan mode)	5		
SIM Method Dwell Time	10 to 60 ms, varied by time segment to maintain minimum cycle time of 6.7 Hz		
EM Gain Factor (SIM Mode)	2		

## Results and discussion

### Scan results



**Figure 2.** Total ion chromatogram (TIC) from the scan analysis of the 25 µg/L standard. The numbers identifying the peaks correspond to the first column in Table 2.

**Table 2.** Peak identifications, calibration results, and deconvoluted library match scores against NIST20 for the scan analysis.

Peak No.	Compound	RT (min)	Tgt m/z	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R <sup>2</sup>	CF	CF Weight	Rel. Std. Error	LMS NIST20	
	Fluorobenzene [ISTD]	2.425	96	77								97	
1	Dichlorodifluoromethane	0.508	85	87	12.5	0.1	25	0.9989	Linear	1/x	17.3	92	
2	Chloromethane	0.615	50	52	14.4	0.25	25	0.9977	Linear	1/x	16.2	97	
3	Chloroethene	0.698	62	64	18.4	0.05	25	0.9995	Linear	1/x	9	91	
4	Bromomethane	0.891	94	96	21.7	1	25	0.9995	Linear	1/x	4.2	96	
5	Ethyl Chloride	0.945	64	66	13.6	0.25	25	0.9995	Linear	1/x	6.5	92	
6	Trichloromonofluoromethane	1.067	101	103	9.6	0.05	25	0.9994	Linear	1/x	9.6	96	
7	Ethyl ether	1.198	74	59	12.8	0.25	25	0.9992	Linear	1/x	11.4	97	
8	1,1-Dichloroethene	1.288	61	96	6.7	0.05	25	0.9993	Linear	1/x	7.3	98	
9	Acetone	1.317	58	43	112.5	1	25	0.9770	Linear	1/x	22.9	87	*
10	Iodomethane	1.350	142	127	14.6	0.05	25	0.9997	Linear	1/x	7.4	99	
11	Carbon disulfide	1.379	76		16.4	0.05	25	0.9997	Linear	1/x	5.7	95	
12	Allyl chloride	1.432	76	41	13.9	0.1	25	0.9982	Linear	1/x	17.2	97	
13	Methylene chloride	1.478	84	49	5.0	0.1	25	0.9996	Linear	1/x	5.1	97	
14	Acrylonitrile	1.572	52	53	16.1	0.5	25	0.9940	Linear	1/x	16.3	90	
15	<i>trans</i> -1,2-Dichloroethylene	1.586	61	96	15.9	0.05	25	0.9991	Linear	1/x	17.5	99	
16	Methyl tert-butyl ether	1.592	73	57	8.3	0.05	25	0.9991	Linear	1/x	9.6	98	
17	1,1-Dichloroethane	1.745	63	65	9.4	0.05	25	0.9998	Linear	1/x	5.2	97	
18	<i>cis</i> -1,2-Dichloroethylene	1.966	61	96	7.9	0.05	25	0.9998	Linear	1/x	6.1	95	
19	2,2-Dichloropropane	1.969	77	79	3.1	0.5	25	0.9994	Linear	1/x	3.7	80	**
20	Propanenitrile	1.993	54	52	14.5	0.5	25	0.9943	Linear	1/x	16.4	67	*
21	2-Propenoic acid, methyl ester	2.008	55	85	12.2	0.1	25	0.9991	Linear	1/x	8.5	97	

Peak No.	Compound	RT (min)	Tgt m/z	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R <sup>2</sup>	CF	CF Weight	Rel. Std. Error	LMS NIST20	
22	Methylacrylonitrile	2.052	67	52	4.6	0.5	25	0.9994	Linear	1/x	4.4	95	
23	Bromochloromethane	2.059	130	128	15.4	0.1	25	0.9946	Linear	1/x	14.2	97	
24	Trichloromethane	2.086	83	85	7.0	0.1	25	0.9989	Linear	1/x	11.5	98	
25	Tetrahydrofuran	2.090	72	71	19.1	0.25	25	0.9959	Linear	1/x	10.3	96	
26	1,1,1-Trichloroethane	2.168	97	99	14.9	0.05	25	0.9995	Linear	1/x	9.6	98	
27	1-Chlorobutane	2.205	56	41	5.1	0.1	25	0.9997	Linear	1/x	6.6	97	
28	1,1-Dichloropropene	2.231	75	110	18.5	0.05	25	0.9980	Linear	1/x	13.8	96	
29	Carbon Tetrachloride	2.235	117	119	8.7	0.1	25	0.9983	Linear	1/x	9.4	96	
30	Benzene	2.315	78	77	10.4	0.05	25	0.9991	Linear	1/x	11.4	94	
31	1,2-Dichloroethane	2.316	62	64	15.5	0.05	25	0.9989	Linear	1/x	9.8	98	
32	Trichloroethylene	2.577	130	132	18.7	0.1	25	0.9981	Linear	1/x	12.4	99	
33	1,2-Dichloropropane	2.671	63	62	10.8	0.1	25	0.9997	Linear	1/x	9	98	
34	Methyl methacrylate	2.713	100	69	8.4	0.1	25	0.9991	Linear	1/x	10.5	98	
35	Dibromomethane	2.722	174	172	13.6	0.1	25	0.9989	Linear	1/x	18	98	
36	Bromodichloromethane	2.785	83	85	14.5	0.1	25	0.9997	Linear	1/x	4.1	98	
37	2-Nitropropane	2.883	43	41	19.4	0.5	25	0.9973	Linear	1/x	16.2	93	
38	Chloromethyl cyanide	2.887	75	77	51.4	1	25	0.9947	Linear	1/x	9.7	63	*
39	cis-1,3-Dichloropropene	2.985	75	110	12.9	0.1	25	0.9956	Linear	1/x	12.4	98	
40	Toluene	3.145	91	92	2.9	0.05	25	0.9995	Linear	1/x	4.3	99	
41	trans-1,3-Dichloropropene	3.239	75	110	7.1	0.05	25	0.9963	Linear	1/x	9.3	98	
42	Ethyl methacrylate	3.283	69	41	9.6	0.05	25	0.9989	Linear	1/x	10.5	98	
43	1,1,2-Trichloroethane	3.328	97	99	11.0	0.1	25	0.9994	Linear	1/x	7.8	98	
44	Tetrachloroethylene	3.410	164	166	10.0	0.1	25	0.9991	Linear	1/x	11.3	91	
45	1,3-Dichloropropane	3.412	76	78	17.9	0.05	25	0.9978	Linear	1/x	10.7	90	
46	Dibromochloromethane	3.524	129	127	6.0	0.1	25	0.9998	Linear	1/x	5.2	98	
47	1,2-Dibromoethane	3.585	109	107	6.9	0.25	25	0.9989	Linear	1/x	9.1	99	
48	Chlorobenzene	3.835	112	114	8.7	0.05	25	0.9951	Linear	1/x	12.8	99	
49	1,1,1,2-Tetrachloroethane	3.875	133	131	10.4	0.1	25	0.9968	Linear	1/x	14.4	96	
50	Ethylbenzene	3.892	91	106	5.6	0.05	25	0.9992	Linear	1/x	4.3	98	
51	m-Xylene	3.953	91	106	7.7	0.05	25	0.9991	Linear	1/x	4.6	99	
52	o-Xylene	4.164	91	106	6.7	0.05	25	0.9995	Linear	1/x	10.8	89	
53	Styrene	4.169	104	103	13.0	0.05	25	0.9972	Linear	1/x	8.8	96	
54	Tribromomethane	4.266	173	171	14.1	0.1	25	0.9993	Linear	1/x	11.2	99	
55	Isopropylbenzene	4.364	105	120	15.9	0.05	25	0.9978	Linear	1/x	6.9	98	
56	p-Bromofluorobenzene [SURR]	4.446	174	176								97	
57	1,1,2,2-Tetrachloroethane	4.521	83	85	9.4	0.1	25	0.9981	Linear	1/x	12.4	97	
58	Bromobenzene	4.530	158	156	11.4	0.1	25	0.9963	Linear	1/x	15.9	97	
59	1,2,3-Trichloropropane	4.548	110	112	8.5	0.25	25	0.9960	Linear	1/x	14.7	84	
60	trans-1,4-Dichloro-2-butene	4.555	89	88	9.9	0.25	25	0.9985	Linear	1/x	10.7	65	**
61	Propylbenzene	4.592	91	120	8.6	0.05	25	0.9989	Linear	1/x	8.1	98	
62	2-Chlorotoluene	4.638	91	126	7.9	0.05	25	0.9993	Linear	1/x	7.3	98	
63	Mesitylene	4.692	105	120	11.6	0.05	25	0.9972	Linear	1/x	8	91	
64	tert-Butylbenzene	4.876	134	91	17.4	0.25	25	0.9954	Linear	1/x	15.5	97	
65	Pentachloroethane	4.881	167	165	13.3	0.1	25	0.9967	Linear	1/x	17.2	86	
66	1,2,4-Trimethylbenzene	4.903	105	120	11.8	0.05	25	0.9975	Linear	1/x	8.4	98	
67	1-Methylpropyl benzene	5.001	105	134	19.0	0.05	25	0.9955	Linear	1/x	11.9	98	

Peak No.	Compound	RT (min)	Tgt m/z	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R <sup>2</sup>	CF	CF Weight	Rel. Std. Error	LMS NIST20	
68	1,3-Dichlorobenzene	5.060	146	148	10.8	0.05	25	0.9979	Linear	1/x	13.3	99	
69	<i>p</i> -Cymene (4-Isopropyltoluene)	5.086	119	134	9.9	0.05	25	0.9994	Linear	1/x	6.9	97	
70	1,4-Dichlorobenzene	5.110	146	148	9.7	0.05	25	0.9979	Linear	1/x	17.2	99	
71	1,2-Dichlorobenzene-D4 [SURR]	5.313	152	150								78	**
72	<i>n</i> -Butylbenzene	5.322	91	92	9.5	0.1	25	0.9956	Linear	1/x	12.9	96	
73	1,2-Dichlorobenzene	5.325	146	148	12.0	0.05	25	0.9993	Quadratic	1/x	12.6	92	
74	Hexachloroethane	5.476	166	164	13.7	0.1	25	0.9979	Linear	1/x	14.4	97	
75	1,2-Dibromo-3-chloropropane	5.775	155	75	5.1	0.25	25	0.9982	Linear	1/x	8.2	98	
76	Nitrobenzene	5.896	77	51	15.6	1	25	0.9981	Linear	1/x	5.5	94	
77	1,2,4-Trichlorobenzene	6.270	180	182	13.5	0.05	10	0.9990	Linear	1/x	15.1	99	
78	1,1,2,3,4,4-Hexachlorobuta-1,3-diene	6.380	225	223	8.6	0.05	25	0.9997	Linear	1/x	9.6	91	
79	Naphthalene	6.413	128	127	7.1	0.05	25	0.9986	Linear	1/x	11.4	99	
80	1,2,3-Trichlorobenzene	6.558	180	182	13.4	0.05	25	0.9942	Linear	1/x	12.5	99	

\* Library match score lower due to low response of compound.

\*\* Library match score lower due to overlapping spectra not completely removed by deconvolution.

### Initial calibration (ICAL) with scan data

The chromatographic parameters used in the method resulted in good separation of the 80 VOC compounds in less than 7 minutes, as shown in Figure 2. While there are overlapping peaks, their response was measured selectively with the quantifier ions chosen. Most compounds had sufficient response to be measured at or below 0.1 µg/L, and exhibit very good linearity. The average calibration range was 0.16 to 25 µg/L with an average R<sup>2</sup> of 0.9978. If necessary, the relative standard error (RSE) value was used to guide removal of the lowest, and in one case highest, calibration points, to achieve an RSE value of <20% (except for acetone). The average Response Factor RSD was <20 for 76 analytes. As expected, polar compounds with higher solubility in water were the worst performers. Acetone is an example, where it also had a contamination issue as observed in the blank, resulting in poor calibration results. A typical example is shown in Figure 3, with the lowest calibrator and calibration curve for iodomethane.

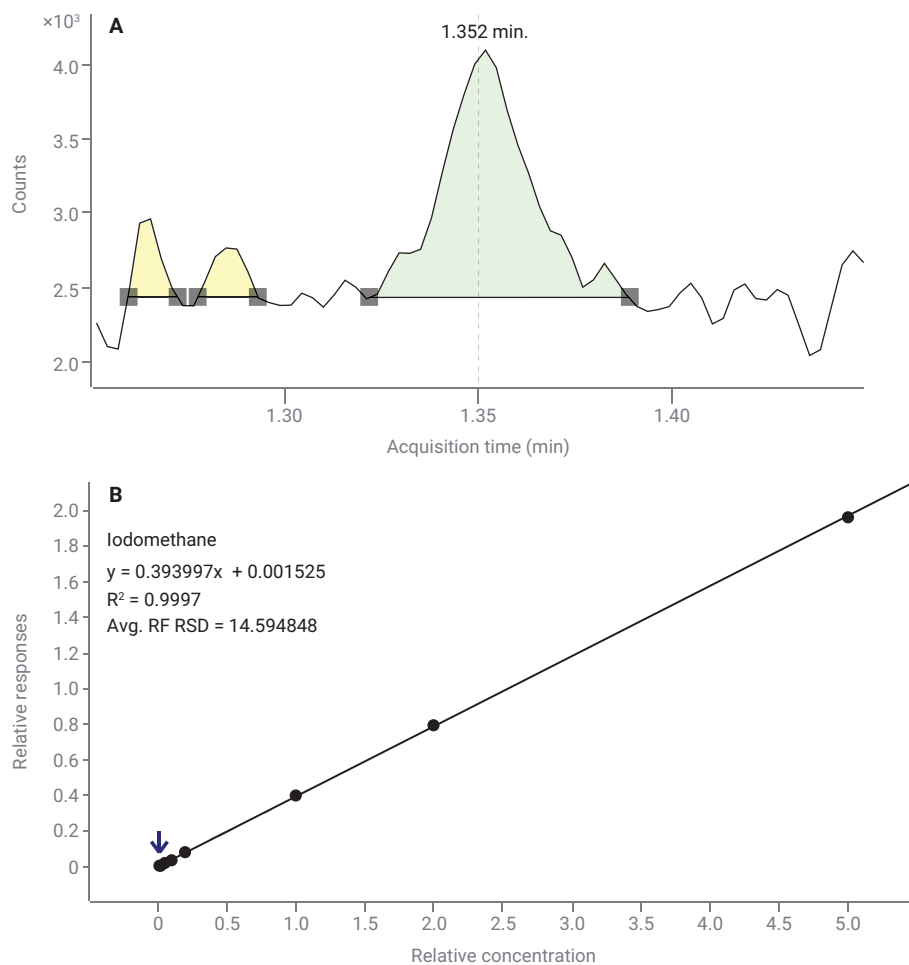


Figure 3. (A) quantifier EIC for iodomethane 0.05 µg/L calibration standard. (B) calibration curve for iodomethane from 0.05 µg/L to 25 µg/L.

## Spectral fidelity

The 25 µg/L VOC standard was analyzed with the MassHunter Unknowns Analysis software, where spectra of the compounds were deconvoluted and searched against the NIST20 library. As seen in Table 2, the library match scores (LMS) are excellent, with an average of 94. There were only six compounds with LMS scores below 90, and these were due to low response and/or interference from overlapping peaks not completely removed by deconvolution. Nitrobenzene (compound 76 in Table 2) gave a very good LMS value of 94. Nitrobenzene reacts readily with hydrogen in a conventional MS source to produce

aniline<sup>4</sup>, resulting in low LMS values typically in the 60s. The HydroInert source greatly reduces in-source reactions with hydrogen, resulting in the high LMS value for nitrobenzene.

## Initial calibration with SIM data

The results of the SIM mode calibration are listed in Table 3. As expected, for most compounds, SIM provided excellent calibration linearity and measurement at or below 0.05 µg/L. The average calibration range was 0.07 to 24 µg/L, with an average R<sup>2</sup> of 0.9990. If necessary, the relative standard error (RSE) value was used to guide removal of the lowest and highest calibration

points, to achieve an RSE value of <20%, and for choosing between a linear or quadratic fit. For some compounds, a linear fit would meet the <20% RSE criteria, but come close to the limit. However, use of a quadratic fit would significantly improve the RSE. For example, *tert*-butylbenzene had an RSE of 18.3 with a linear fit, but changing to quadratic lowered the RSE to 8.1. Similar improvements were seen with some of the other substituted benzenes as well. As observed with the scan data calibration, the average response factor RSD was <20 for 76 analytes.

## SIM results

**Table 3.** Calibration results, and method detection limits (MDL) using SIM acquisition.

Peak No.	Compound Name	RT (min)	Tgt m/z	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R <sup>2</sup>	CF	CF Weight	Rel. Std. Error	Conc. for MDL	MDL (µg/L)
	Fluorobenzene [ISTD]	2.425	96	77									
1	Dichlorodifluoromethane	0.508	85	87	15.3	0.05	25	0.9994	Linear	1/x	11.6	0.10	0.011
2	Chloromethane	0.615	50	52	7.3	0.1	25	0.9997	Linear	1/x	8.4	0.10	0.022
3	Chloroethene	0.698	62	64	4.1	0.05	25	0.9998	Linear	1/x	4.7	0.05	0.008
4	Bromomethane	0.891	94	96	4.1	0.05	25	0.9999	Linear	1/x	4.4	0.10	0.029
5	Ethyl Chloride	0.945	64	66	4.5	0.05	25	0.9998	Linear	1/x	4.7	0.05	0.010
6	Trichloromonofluoromethane	1.067	101	103	4.1	0.05	25	0.9997	Linear	1/x	4.3	0.05	0.008
7	Ethyl ether	1.198	74	59	6.4	0.05	25	0.9994	Linear	1/x	11	0.05	0.017
8	1,1-Dichloroethene	1.288	61	96	5.9	0.05	25	0.9996	Linear	1/x	5.3	0.05	0.006
9	Acetone	1.317	58	43	102.2	1	10	0.9994	Linear	1/x	3.5	[cont]	
10	Iodomethane	1.350	142	127	3.3	0.05	25	0.9992	Linear	1/x	4.8	0.05	0.006
11	Carbon disulfide	1.379	76		12.6	0.1	25	0.9994	Linear	1/x	4.6	0.05	0.003
12	Allyl chloride	1.432	76	41	4.9	0.05	25	0.9997	Linear	1/x	6.4	0.05	0.014
13	Methylene chloride	1.478	84	49	12.2	0.1	25	0.9999	Linear	1/x	5.2	0.05	0.007
14	Acrylonitrile	1.572	52	53	8.3	0.1	25	0.9999	Linear	1/x	5.4	[0.25]	
15	<i>trans</i> -1,2-Dichloroethylene	1.586	61	96	7.1	0.05	25	0.9997	Linear	1/x	5	0.05	0.007
16	Methyl <i>tert</i> -butyl ether	1.592	73	57	4.2	0.05	25	0.9995	Linear	1/x	7.5	0.05	0.003
17	1,1-Dichloroethane	1.745	63	65	3.7	0.05	25	0.9998	Linear	1/x	4.6	0.05	0.003
18	<i>cis</i> -1,2-Dichloroethylene	1.966	61	96	10.1	0.05	25	0.9996	Linear	1/x	7.3	0.05	0.007
19	2,2-Dichloropropane	1.969	77	79	3.6	0.05	25	0.9999	Linear	1/x	4.2	0.10	0.017
20	Propanenitrile	1.993	54	52	5.0	0.25	25	0.9996	Linear	1/x	4.3	[0.25]	
21	2-Propenoic acid, methyl ester	2.008	55	85	11.0	0.05	25	0.9996	Linear	1/x	14.8	0.10	0.029
22	Methylacrylonitrile	2.052	67	52	7.0	0.05	25	0.9988	Linear	1/x	11.4	0.10	0.032
23	Bromochloromethane	2.059	130	128	4.2	0.25	25	0.9991	Linear	1/x	3.5	0.10	0.019
24	Trichloromethane	2.086	83	85	12.2	0.25	10	0.9997	Linear	1/x	1.8	0.05	0.011
25	Tetrahydrofuran	2.090	72	71	3.3	0.05	25	0.9999	Linear	1/x	4.2	0.05	0.030

Peak No.	Compound Name	RT (min)	Tgt MZ	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R <sup>2</sup>	CF	CF Weight	Rel. Std. Error	Conc. for MDL	MDL (µg/L)
26	1,1,1-Trichloroethane	2.168	97	99	4.9	0.05	25	0.9995	Linear	1/x	5.5	0.05	0.007
27	1-Chlorobutane	2.205	56	41	11.7	0.05	25	0.9997	Linear	1/x	7.3	0.05	0.007
28	1,1-Dichloropropene	2.231	75	110	7.3	0.05	25	0.9960	Linear	1/x	16.7	0.05	0.007
29	Carbon Tetrachloride	2.235	117	119	7.5	0.05	25	0.9974	Linear	1/x	13.1	0.05	0.015
30	Benzene	2.315	78	77	4.0	0.05	25	0.9998	Linear	1/x	3.5	0.05	0.004
31	1,2-Dichloroethane	2.316	62	64	3.0	0.05	25	0.9993	Linear	1/x	3.3	0.05	0.005
32	Trichloroethylene	2.577	130	132	5.6	0.05	25	0.9993	Linear	1/x	6.9	0.05	0.006
33	1,2-Dichloropropane	2.671	63	62	4.9	0.05	25	0.9998	Linear	1/x	4.6	0.05	0.011
34	Methyl methacrylate	2.713	100	69	9.4	0.05	25	0.9994	Linear	1/x	10.6	0.05	0.033
35	Dibromomethane	2.722	174	172	5.7	0.05	25	0.9996	Linear	1/x	6.3	0.05	0.009
36	Bromodichloromethane	2.785	83	85	3.0	0.05	25	0.9999	Linear	1/x	3.8	0.05	0.011
37	2-Nitropropane	2.883	43	41	8.9	0.1	25	0.9998	Linear	1/x	8.6	0.10	0.041
38	Chloromethyl cyanide	2.887	75	77	81.1	0.25	25	0.9997	Quadratic	1/x	7.6	[0.25]	
39	cis-1,3-Dichloropropene	2.985	75	110	3.8	0.05	10	0.9994	Linear	1/x	3.6	0.05	0.003
40	Toluene	3.145	91	92	5.2	0.05	25	0.9997	Linear	1/x	4	0.05	0.003
41	trans-1,3-Dichloropropene	3.239	75	110	6.3	0.05	25	0.9956	Linear	1/x	12	0.05	0.005
42	Ethyl methacrylate	3.283	69	41	4.6	0.05	25	0.9990	Linear	1/x	4.7	0.05	0.008
43	1,1,2-Trichloroethane	3.328	97	99	5.4	0.05	25	0.9998	Linear	1/x	2.5	0.05	0.034
44	Tetrachloroethylene	3.410	164	166	5.9	0.05	25	0.9994	Linear	1/x	9.9	0.05	0.005
45	1,3-Dichloropropane	3.412	76	78	5.8	0.05	25	0.9988	Linear	1/x	5.7	0.05	0.007
46	Dibromochloromethane	3.524	129	127	4.2	0.05	25	0.9999	Linear	1/x	4.6	0.05	0.008
47	1,2-Dibromoethane	3.585	109	107	8.1	0.05	25	0.9993	Linear	1/x	3.6	0.05	0.005
48	Chlorobenzene	3.835	112	114	6.6	0.05	25	0.9948	Linear	1/x	12.9	0.05	0.002
49	1,1,1,2-Tetrachloroethane	3.875	133	131	5.0	0.05	25	0.9991	Linear	1/x	9.1	0.05	0.007
50	Ethylbenzene	3.892	91	106	5.0	0.05	25	0.9994	Linear	1/x	4.7	0.05	0.005
51	m-Xylene	3.953	91	106	4.6	0.05	25	0.9996	Linear	1/x	4.2	0.05	0.001
52	o-Xylene	4.164	91	106	6.5	0.05	25	0.9999	Linear	1/x	4.9	0.05	0.004
53	Styrene	4.169	104	103	7.1	0.05	25	0.9988	Linear	1/x	6	0.05	0.005
54	Tribromomethane	4.266	173	171	5.4	0.05	25	0.9999	Linear	1/x	4.7	0.05	0.003
55	Isopropylbenzene	4.364	105	120	6.0	0.05	25	0.9981	Linear	1/x	6.2	0.05	0.004
56	p-Bromofluorobenzene [SURR]	4.446	174	176									
57	1,1,2,2-Tetrachloroethane	4.521	83	85	8.0	0.05	25	0.9999	Quadratic	1/x	4.8	0.05	0.006
58	Bromobenzene	4.530	158	156	7.1	0.05	25	0.9998	Linear	1/x	5.4	0.05	0.003
59	1,2,3-Trichloropropane	4.548	110	112	8.2	0.05	25	0.9970	Linear	1/x	12.2	0.05	0.024
60	trans-1,4-Dichloro-2-butene	4.555	89	88	13.0	0.25	25	0.9999	Linear	1/x	2.2	[0.25]	
61	Propylbenzene	4.592	91	120	5.4	0.05	25	0.9988	Linear	1/x	5.8	0.05	0.008
62	2-Chlorotoluene	4.638	91	126	4.1	0.05	25	0.9996	Linear	1/x	4.7	0.05	0.006
63	Mesitylene	4.692	105	120	5.9	0.05	25	0.9969	Linear	1/x	8.6	0.05	0.008
64	tert-Butylbenzene	4.876	134	91	10.5	0.05	25	0.9997	Quadratic	1/x	8.1	0.05	0.004
65	pentachloroethane	4.881	167	165	6.6	0.05	25	0.9953	Linear	1/x	6.6	0.05	0.009
66	1,2,4-Trimethylbenzene	4.903	105	120	6.8	0.05	25	0.9985	Linear	1/x	5.3	0.05	0.007
67	1-Methylpropyl benzene	5.001	105	134	5.3	0.05	10	0.9995	Linear	1/x	5.1	0.05	0.004
68	1,3-Dichlorobenzene	5.060	146	148	5.0	0.05	25	0.9990	Linear	1/x	7.6	0.05	0.003
69	p-Cymene (4-Isopropyltoluene)	5.086	119	134	5.1	0.05	25	0.9994	Linear	1/x	8.2	0.05	0.009
70	1,4-Dichlorobenzene	5.110	146	148	5.4	0.05	25	0.9985	Linear	1/x	8.5	0.05	0.004
71	1,2-Dichlorobenzene-D4 [SURR]	5.313	152	150									
72	n-Butylbenzene	5.322	91	92	9.8	0.05	25	0.9997	Quadratic	1/x	6.3	0.05	0.012



Peak No.	Compound Name	RT (min)	Tgt MZ	Q1	Avg. RF RSD	CF Limit Low (µg/L)	CF Limit High (µg/L)	CF R <sup>2</sup>	CF	CF Weight	Rel. Std. Error	Conc. for MDL	MDL (µg/L)
73	1,2-Dichlorobenzene	5.325	146	148	5.4	0.05	10	0.9995	Linear	1/x	6.3	0.05	0.003
74	Hexachloroethane	5.476	166	164	5.0	0.05	25	0.9996	Linear	1/x	8.2	0.05	0.008
75	1,2-Dibromo-3-chloropropane	5.775	155	75	15.2	0.05	25	0.9991	Linear	1/x	7.9	0.05	0.017
76	Nitrobenzene	5.896	77	51	8.5	0.25	25	0.9992	Linear	1/x	9.3	[0.25]	
77	1,2,4-Trichlorobenzene	6.270	180	182	6.1	0.05	10	0.9996	Linear	1/x	5.5	0.05	0.007
78	1,1,2,3,4,4-Hexachlorobuta-1,3-diene	6.380	225	223	13.3	0.05	25	0.9996	Linear	1/x	5.9	0.05	0.006
79	Naphthalene	6.413	128	127	7.9	0.05	25	0.9989	Linear	1/x	8.9	0.05	0.003
80	1,2,3-Trichlorobenzene	6.558	180	182	4.0	0.05	10	0.9996	Linear	1/x	4.9	0.05	0.006

Figure 4 shows a typical example with the lowest calibrator and calibration curve for iodomethane. The improved signal-to-noise ratio provided by SIM, relative to that shown in Figure 3, is clear.

### Method detection limits

An MDL study was performed after completion of the initial calibration. Eight trials were performed at the lowest level of calibration, 0.05 µg/L. The calculated MDLs were obtained by applying the formula shown in Equation 1. For compounds with higher reporting limits, eight trials were performed at the concentration of 0.1 µg/L. Table 3 lists the calculated MDLs for 80 VOCs. Six compounds had insufficient response, even at the 0.1 µg/L level, so the lowest calibration level used is listed instead in bold and square brackets. As noted in the scan results, acetone also had a contamination issue as observed in the blank, resulting in poor calibration results. The average MDL for the 80 compounds was 0.026 µg/L.

**Equation 1.** Formula for MDL calculations.

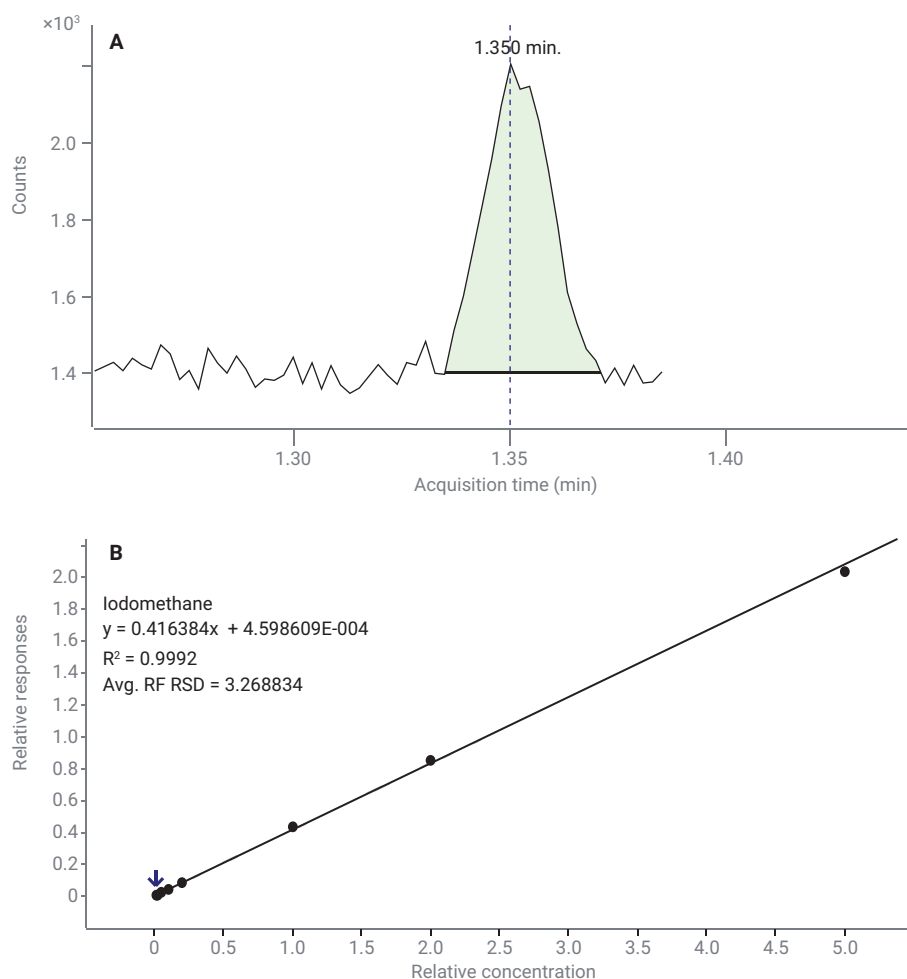
$$\text{MDL} = s \cdot t(n - 1, 1 - \alpha = 99) \\ = s \cdot 2.998$$

Where:

$t(n - 1, 1 - \alpha)$  = t value for the 99% confidence level with  $n - 1$  degrees of freedom

$n$  = number of trials (8)

$s$  = standard deviation of the eight trials

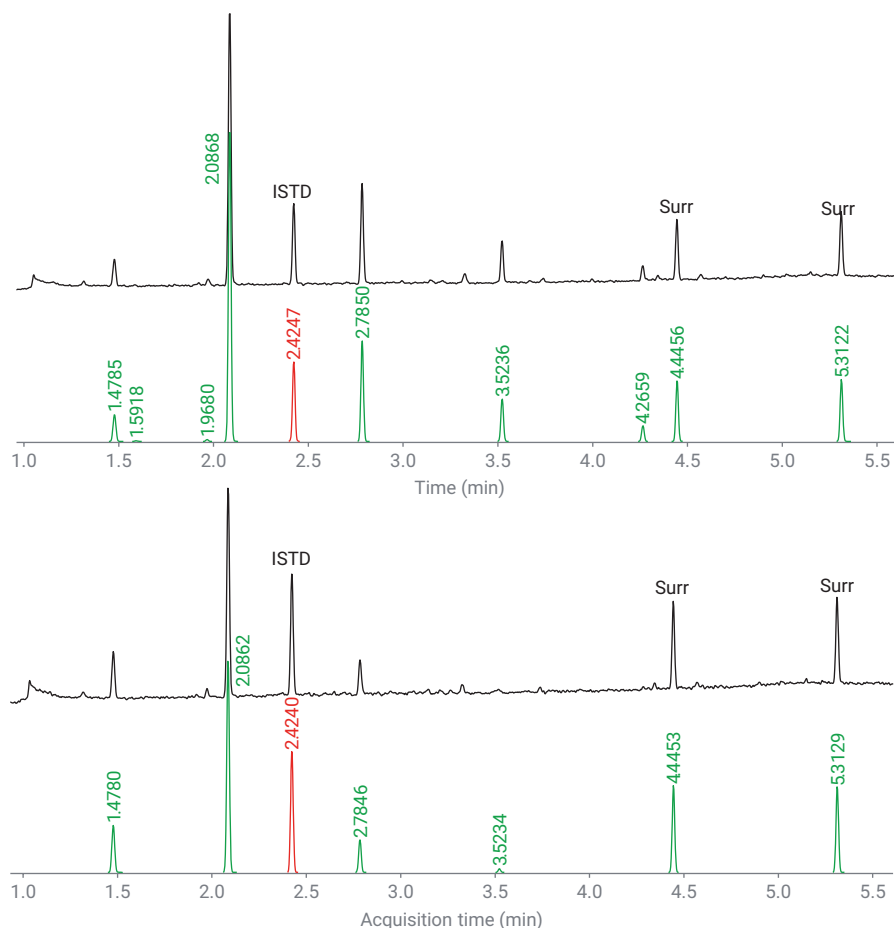


**Figure 4.** SIM results for iodomethane. (A) quantifier EIC for iodomethane 0.05 µg/L calibration standard. (B) calibration curve for iodomethane from 0.05 µg/L to 25 µg/L.

## VOCs found in drinking water

Samples of municipal tap water from sources in the state of Pennsylvania were analyzed using both the scan and SIM methods. Several VOCs were identified with MassHunter Unknowns Analysis and by searching the deconvoluted spectra against the NIST20 library. The chromatograms from two of the samples are shown in Figure 5. The concentration of VOCs was determined using MassHunter Quantitative Analysis, with both the scan and SIM calibrations. The results are presented in Table 4.

Trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane (collectively known as the trihalomethanes) are very common in municipal water treated with chlorine for disinfection purposes. They are the products of reaction between chlorine and naturally occurring humic and fulvic acids, often present in source water. All trihalomethanes were confirmed in both samples with precisely matching retention times, qualifier ion ratios, and, except for tribromomethane, with good LMS search results. As expected, LMS values decrease with decreasing concentration of the analyte. The *cis*-1,2-dichloroethylene and tetrachloroethylene are commonly found at trace levels in ground water from areas with a history of industrial activity. Methyl *tert*-butyl ether (MTBE) was an additive to gasoline several years ago, used in response to federal mandates requiring specified levels of organic oxygen in gasoline. Its use was later banned when it began showing up in ground water as the result of leaking underground storage tanks at gasoline stations.



**Figure 5.** TIC (black) and deconvolution component (green) chromatograms of tap water samples. ISTD is shown in red. Top: Sample from Eastern Pennsylvania. Bottom: Sample from Southeastern Pennsylvania.

**Table 4.** Results from analysis of tap water samples.

Name	RT (min)	Eastern PA			Southeastern PA		
		Scan	Scan	SIM	Scan	Scan	SIM
		LMS NIST20	Conc. (µg/L)	Conc. (µg/L)	LMS NIST20	Conc. (µg/L)	Conc. (µg/L)
Methyl <i>tert</i> -butyl ether	1.592	56	0.08	0.08			
<i>cis</i> -1,2-Dichloroethylene	1.968	71	0.19	0.20			
Trichloromethane	2.087	98	43.47	44.08	97	21.03	20.90
Bromodichloromethane	2.785	98	21.81	22.07	92	4.82	4.85
Tetrachloroethylene	3.410			0.05			
Dibromochloromethane	3.524	98	11.34	10.80	68	0.69	0.69
Tribromomethane	4.266	97	3.97	3.71			0.02

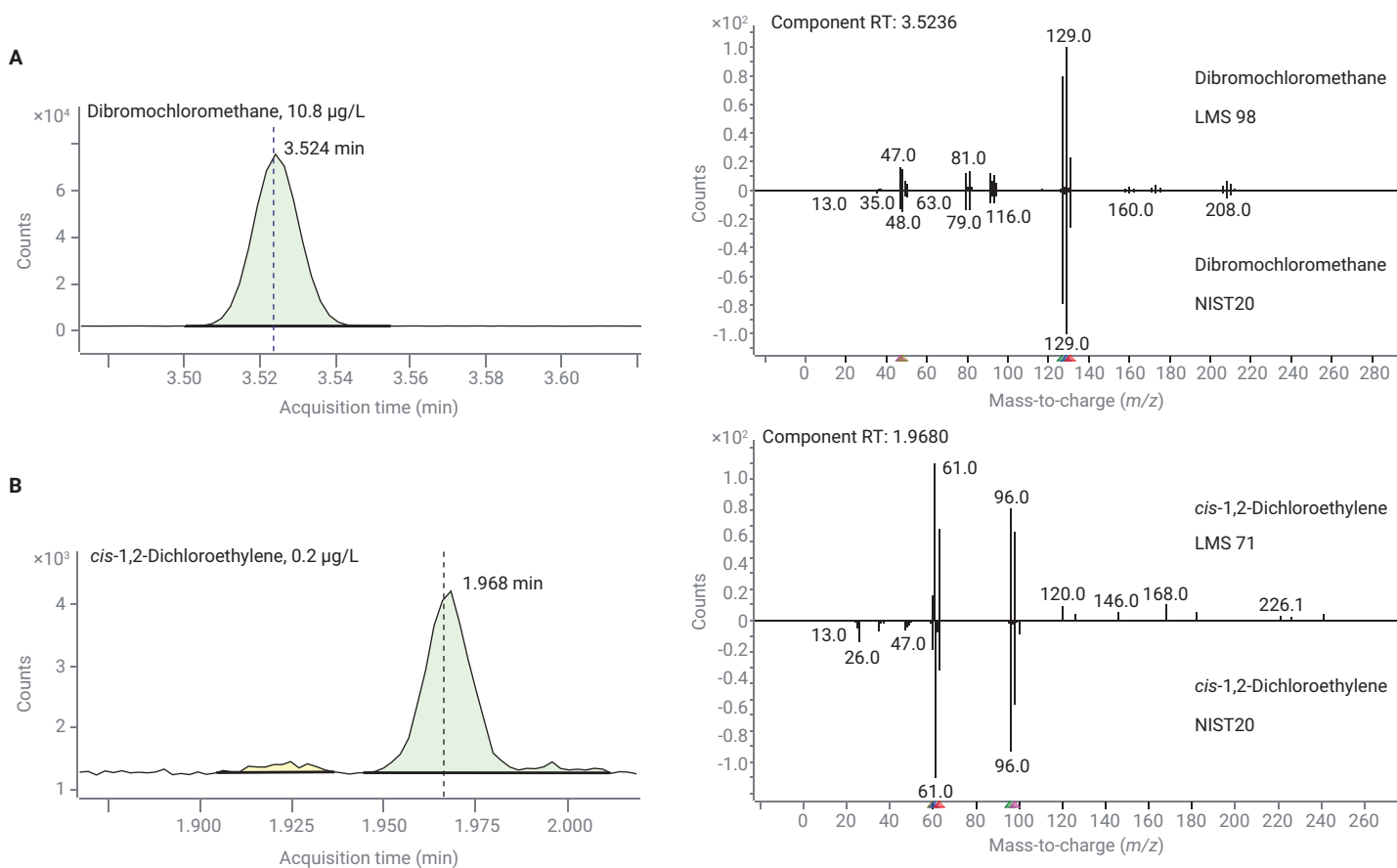
Figure 6 shows the benefits of using both the scan and SIM methods on tap water samples. Spectral matching provides added confidence in the identification of compounds in the water samples. The scan data were processed in Agilent MassHunter Quantitative Unknowns Analysis software, which provides streamlined automated deconvolution and library searching. Previous approaches to processing scan data for library searching rely on comparing a baseline-subtracted apex spectrum of a peak to reference spectra. That approach can work well with a limited number of peaks, to identify

when there are no chromatographic interferences with the peak. However, samples containing significant levels of overlapping chromatographic peaks can interfere with the process, making analyte identification challenging. The automated deconvolution and library searching in MassHunter Unknowns Analysis greatly simplifies the processing of spectral data.

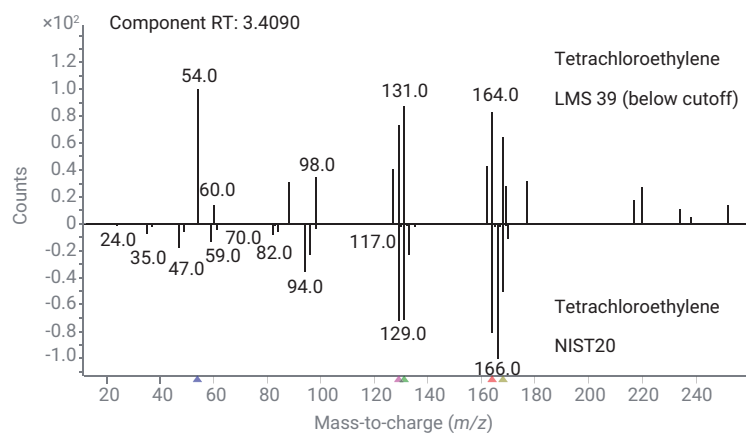
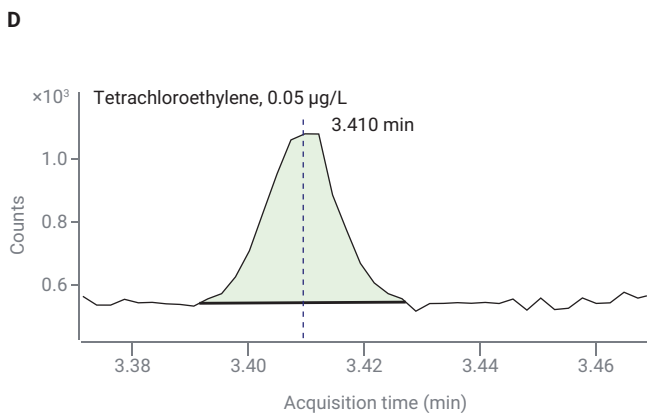
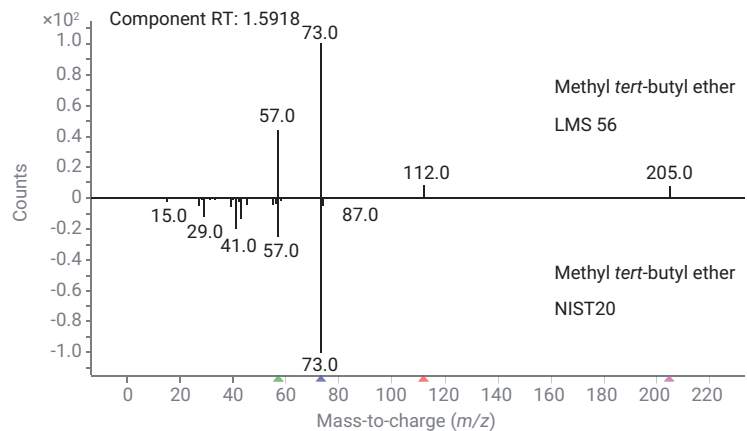
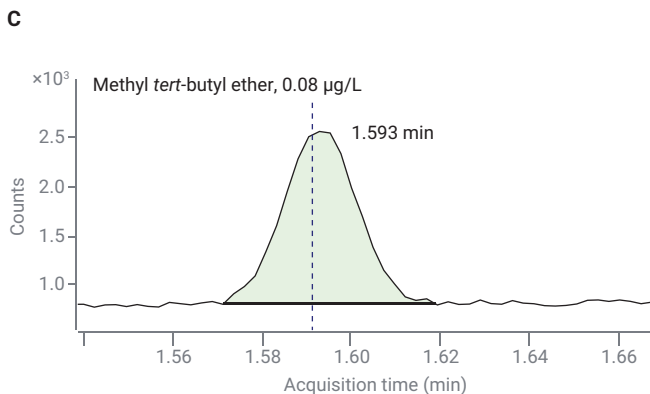
Figure 6 shows the extracted SIM quantifier ions and deconvoluted spectra for four of the seven VOCs found in the Eastern PA water sample. Dibromochloromethane [A] is confidently

identified with an RT that precisely matches that in the calibration table, an acceptable ratio of the qualifier to quantifier responses (not shown), and a very high library match score.

As the concentration of an analyte decreases, the signal-to-noise ratio in the both the spectra and quantifier chromatograms also decrease. In Figure 6, the spectral information is useful down to about 0.1 µg/L. The SIM data, which identifies using precise RT matching and the ratio of the qualifier to quantifier response can be used to lower levels.



**Figure 6.** Quantifier ion extracted chromatograms from the SIM run and corresponding deconvoluted spectra from scan runs of the Eastern PA tap water sample (continued on next page).



## Conclusion

The Agilent 8890/5977C GC/MSD system coupled with an Agilent 8697 headspace sampler was successfully used with hydrogen carrier gas for the analysis of volatile organic compounds (VOCs) in drinking water. While helium remains the preferred carrier gas for GC/MS, hydrogen has been shown here as a viable alternative if problems with the price and/or availability of helium arise. One of the key components

contributing to system performance is the new HydroInert source, which was designed specifically for hydrogen use. In addition to the new source, chromatographic conditions were optimized to provide separation of 80 volatile compounds in 7 minutes.

The results of the scan mode evaluation demonstrated excellent spectral matching against the NIST20 library, and excellent calibration linearity with an average range of 0.16 to 25 µg/L.

The results of the SIM mode evaluation demonstrated excellent calibration linearity with an average range of 0.07 to 25 µg/L, and an average MDL for the 80 compounds of 0.026 µg/L. The method described here gives results comparable to those observed with helium-based headspace methods in references 2 and 3.

The utility of the system was then demonstrated analyzing municipal tap water samples.

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